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# In-line particle size assessment of polymer suspensions during processing

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## ABSTRACT

The validation and the operating window of an in-line rheo-optical slit die coupled to a prototype single/twin-screw mini-extrusion system are reported. This experimental set-up is able to perform in-situ rheological measurements, together with Small Angle Light Scattering (SALS) and Polarized Optical Microscopy (POM), thus enabling the structural characterization of materials during extrusion. The optical validation focuses on particle sizing and is performed using standard size particles suspended in a Newtonian polydimethylsiloxane (PDMS) matrix. The outcome is a map of the range of particle sizes and concentrations that can be measured with the two complementary in-line optical techniques. The techniques are then applied to study the morphological development in PMMA/PS blends, in order to screen for their applicability to commercial systems. Thus, limitations of POM and SALS for the characterization of industrial materials are also indicated.

## 1. Introduction

The processability and subsequent performance under service conditions of plastics products depend on the interplay between material characteristics (particularly the viscoelastic behavior), processing conditions and flow-induced morphology. As increasingly more sophisticated polymer systems are being developed and times-to-market need to be minimized, it is important to make available fast response and informative characterization tools using small amounts of sample. In-line/on-line measurements during compounding or processing are particularly attractive for this purpose. On-line rheometry [1–4] can provide efficient rheological characterization of complex materials, but it only conveys an indirect indication of the type and size of the nano- or micro-structures being formed during flow. In the case of on-line sampling [5,6], the actual analysis is performed off-line, for example by X-ray diffraction or electron microscopy, which are time consuming. Therefore, in-situ structural characterization together with on-line rheological characterization is greatly needed.

Rheo-optical methods which merge rheological and optical characterizations have been developed to access a wide range of length scales in various flowing complex fluids [7–10]. Among rheo-optical techniques, Small Angle Light Scattering (SALS) and Polarized Optical Microscopy (POM) are particularly attractive as they give spatial information on flow-induced structures [7,8], in contrast to polarimetry based optical techniques [9,10]. However, despite its potential application to assess and quantify flow-induced morphologies, the use of SALS in extrusion has been limited [11]. For example, when sensing in-line particle size, several factors may jeopardize the measurement, such as machine vibration, material contamination, large concentration of particles or sample thickness, contributing to multiple scattering and inherent systematic

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errors. While SALS provides statistical information on the bulk, POM can explore only a rather small region of the flow [8], for instance near the walls or in the middle of a slit channel. POM gives access to objects larger than 1 micron, whereas SALS permits measurement of sizes below the micron scale. High enough contrast in the refractive indices of the fluid components is needed in POM, whereas this will promote multiple scattering in SALS.

In-line light scattering studies of polymer blend morphology using a slit die with an optical window coupled to an extruder started over a decade ago [12–14]. On-line light scattering experiments at various possible locations along the barrel of the extruder have also been performed [15,16]. However, these experimental set-ups do not allow for in situ rheological measurements or only give approximated (no pressure correction) in-line viscosity data. Furthermore, the operational windows of these arrangements were not presented, and as such their industrial applicability remains unclear.

This contribution presents a rheo-optical slit die able to perform SALS and POM measurements, as well as capillary-slit experiments, which is coupled to a prototype single/twin-screw mini-extrusion system of modular construction, with well-controlled outputs in the range 30–300 g/h. The rheological validation of the system has been presented elsewhere [17]. The optical validation is performed using small and large volume fractions of standard size particles suspended in a Newtonian polydimethylsiloxane (PDMS) matrix. The outcome is a map of the range of particle sizes and concentrations that can be measured with the two complementary in-line optical techniques. The techniques are then applied to study the morphological development in PMMA/PS blends, in order to screen for their applicability to commercial systems. Thus, limitations of POM and SALS for the characterization of industrial materials will also be discussed.

## 2. Theoretical background

### 2.1. Mie's and Debye-Bueche's theories

Light is scattered when the size of a particle is of the same order of magnitude as the light wavelength and when the refractive indices of particle and surroundings are dissimilar. In a light scattering experiment, the intensity of scattered light is measured as a function of the scattering vector $q$. The latter is experimentally determined from the azimuthal scattering angle, $\theta$, and the wavelength of the laser light, $\lambda$, through the following relationship:

$$q = \frac{4\pi n_0 \sin(\theta/2)}{\lambda} \tag{1}$$

where $n_0$ is the refractive index of the sample. Scattering from the shape of objects and from the structure or arrangement of objects can contribute to the total scattering [7]. In principle, particle size and shape can be measured through a form factor $P(q)$, and structural arrangement under flow can be assessed through a structure factor $S(q)$. Among the several theories that can describe $P(q)$, Mie's [18,19] and Debye-Bueche's [20] were selected and are described below.

Mie's theory [18,19] describes light scattering by particles of any size, irrespective of the incident light wavelength. It provides an exact solution for the scattering of a plane monochromatic wave by an isotropic homogeneous sphere of arbitrary size, embedded in an isotropic medium.

Mie's theory is a powerful tool to appraise the size (or refractive index) of spheres, because the scattering pattern of the latter is very sensitive to changes in size (or refractive index). If the refractive index is known, a comparison of the measured light scattering pattern with that predicted by the theory allows an estimation of particle size. Although numerical computations are required [21], several codes are currently commercially available to compute the Mie scattering of a single homogeneous sphere, a cluster of spheres, a cylinder and other systems [22].

The Debye-Bueche's [20] theory is valid for Rayleigh-Gans-Debye scattering conditions [21], assuming that isotropic scattering objects are sufficiently small relative to light wavelength, and that the interface with the continuous medium is sharp. The theory can also be used to estimate size from light scattering patterns, as it relates the $q$ dependence of the scattered light intensity to structure by:

$$I(q) = C\langle\eta^2\rangle a_c^3 S(qa_c) \tag{2}$$

where $C$ is a constant, $\langle\eta^2\rangle$ is the mean square fluctuation of scattering contrast, $a_c$ is a correlation distance that can be related to particle size and $S$ is a scaling function defined by [23]:

$$S(qa_c) = \frac{1}{\left(1 + a_c^2 q^2\right)^2} \tag{3}$$

Under these assumptions, Eq. 3 links quantitatively domain size with correlation distance. The theory is far easier to use than Mie's theory and was successfully applied to particle sizing in rheo-optical experiments [7,8,11–14].

### 2.2. Multiple scattering

It should be noted that the theories discussed above cover single scattering, i.e., the incident beam is only scattered once within the optical path in the sample. This is a good approximation for very low particle concentrations or small sample thicknesses. In other situations where multiple scattering occurs, computation of particle size using the above theories without corrections inherently delivers sizes smaller than the real ones [21]. Rusu [24] proposed the following empirical criterion to define the inception of multiple scattering:

$$C_{vol}\frac{h}{8a} \le 0.2 \tag{4}$$

where $C_{vol}$ is the volume fraction of spherical particles, $h$ is the sample thickness and $a$ the radius of the sphere.

Ishimaru [25] and van de Hulst [26] reviewed comprehensively multiple scattering theory. For particles larger than light wavelength and concentrations involving multiple scattering, quantitative results can be obtained from Silberberg and Kuhn's theory [27], presuming the existence of a small difference in the refractive index of the phases. A generalization of Hartel's theory, valid in the Mie' scattering